DISCUSSION

Species and Zonal Differences in t-PCBs

Sedimentary concentrations revealed no significant seasonal differences within zones. This reflects sediments' ability to integrate contaminant loads over long time scales. Among zone differences were observed and likely attributed to both sediment characteristics such as carbon content and proximity to source. Highest concentrations of PCBs in Zones 3 and 4 suggest greater inputs due to proximity to both non-point and point sources in the urbanized and industrialized sectors adjacent to these zones (Frithsen et al., 1995). These data reflect earlier collections characterizing sedimentary contaminants in the Delaware River and its tributaries (e.g., Costa et al, 1995; Hartwell et al., 2001; Velinsky and Ashley, unpublished data).

In general, trends in sedimentary PCB inventories between zones were reflected in the concentrations of biota collected within each region. However, concentrations of PCB varied considerably within a zone and this variability did not diminish upon lipid normalization of concentrations. This may be due to differing habitat uses by species within a zone, especially in zones where sediment contamination was more heterogeneous (Zones 3 and 4). This may also be due to variability among individuals in their feeding regimes. For example, though catfish have more limited ranges than perch, they may undergo small scale migrations within a zone, moving into and out of shallow areas or into tributaries (e.g., the Schuylkill River), where differing contaminant regimes may exist.

Quantifying Trophic Transfer through BCFs, BSAFs and PPRs

Bioconcentration factors increased with K_{ow} for all biota samples (Figs. 40-43). The average log BCF for total PCBs was similar throughout the estuary for all biota groups (Table 15). Using filtrate PCB concentrations presents a source of bias as actual dissolved concentrations may be overestimated due to the contribution of non-filterable colloids in total dissolved PCB values, thereby underestimating the bioconcentration factor (Baker and Eisenreich 1990). The contribution of the colloidal fraction to total dissolved PCBs was calculated using:

$$\mathbf{C_d/C_t = 1/1+((K_{ow} * DOC)/10^6)}$$

where DOC is the dissolved organic carbon concentration (kg carbon/ L water) in the Delaware River. The truly dissolved phase is on average ~18% of the filtrate concentration, resulting in a BCF underestimation. Most BCF calculations in the literature do not correct for the colloid fraction contribution, and for that reason BCF values presented in this paper are based on filtrate PCB concentrations.

With increasing hydrophobicity contaminants may adsorb more strongly to particulate matter. Therefore chemicals with large octanol-water partitioning coefficients will not be as readily bioavailable (Mackay and Fraser 2000). Regression analysis showed a positive relationship between bioconcentration and K_{ow} for all biota groups (Figs. 40-43), for channel catfish, white perch, prey fish, and invertebrates (P>0.001). Although bioconcentration factors vary based on K_{ow}, the average log BCF value for biota throughout the study area remains relatively constant, indicating it is possible to apply a universal log BCF value of 7 to the Delaware system.

In order to evaluate the influence of hydrophobicity on bioaccumulation, BSAF values were plotted against log K_{ow} and both linear and quadratic regression analyses were performed for each group of biota, with all zones and seasons included (Figs. 44-47). The parabolic function (P<0.0001 for channel catfish and white perch) better explained the relationship than the linear function, indicating that the bioavailability of chlorinated biphenyls to organisms initially increased and then decreased with increasing hydrophobicity. To address variation among trophic level, BSAF values based on total PCBs for all species are close to the mean of species-specific median BSAF values of 5.1 as shown in a box and whisker plot (Fig. 28), exhibiting similarity in BSAFs between species with comparable habitats. Previous studies have shown that similarity in chemical exposure for benthic species may allow for the application of sediment quality criteria for habitat groups (Tracey and Hansen 1996).

The observed trends in biota BSAF factors are similar to previously reported declines in bioavailability with increasing K_{ow} (Shaw and Connell 1984; Tracey and Hansen 1996; Maruya and Lee 1998). PCBs with K_{ow}s >7 have been shown to have reduced bioavailability, possibly due to problems with membrane permeability or assimilation efficiency (Gobas et al. 1988; Tracey and Hansen 1996; Kannan et al. 1997; Fisk et al. 1998).

Life history of an organism should be considered when grouping of species with similar habitats. Although both species are demersal predators, channel catfish and white perch exhibit a variation in accumulation of extremely hydrophobic PCB congeners present in the lower zones as previously shown. This may be due to migratory patterns as white perch migrate throughout the estuary while channel catfish remain in a small home range and have increased contact with the hydrophobic congeners. This is an important consideration in systems with point sources and sharp pollutant chemical gradients. However, we found that these variations in congener patterns do not affect the BSAF values based on total PCBs of these benthic species.

Biota samples from urbanized estuaries have elevated concentrations of PCBs corresponding to the highly urbanized zone 3 as shown previously. BSAFs do not vary with PCB concentration levels (Table 15). Although BSAFs vary within the river, the average BSAF is similar for all species. The spatial heterogeneity of PCB levels in sediment from the river leads to concerns whether natural variability would adequately be addressed using these BSAF values.

Tracey and Hansen (1996) calculated BSAF values among habitat groups from field data with median BSAFs of 2.2 and 1.4 for the benthically-coupled species of channel catfish and white perch respectively, which are lower than the BSAF of 5.1 found in this study. BSAF values express exposure levels from sediment. The higher BSAF values obtained in this study, suggest that the organisms are more efficient at bioaccumulation of PCBs, exposure is originating from some other source than sediment, or that the sediment samples are not representative of the study area. The sediment sites were randomly selected throughout each of the four zones, with little sampling occurring in the flanks of the river, and may not adequately represent the spatial heterogeneity in the river. Organisms may not be feeding in the channels, but possibly closer to shorelines or in hot spots of contamination the river. Prey items such as small fish and macro invertebrates may be accumulating high levels of contaminants from tributaries, marsh areas, or flanks of the river then dispersing throughout the main steam of the river where they may be preyed upon. It is also possible that organisms are not accumulating a large proportion of contaminants from sediment, but from dissolved or particulate PCBs in the water column or ingestion of contaminated prey items as previously mentioned.

All organisms in this food web are benthic species; therefore they may not be directly comparable to previous work on the kinetics of PCB transport throughout food webs containing many trophic levels. As omnivorous feeders, the trophic position of channel catfish is difficult to characterize (VanderZanden and Rasmussen 1996), as demonstrated by gut content analysis which included a variety of items such as algae and insects. White perch stomach contents were mainly comprised of the invertebrate *Gammarus duebeni* (Horwitz et al. 2002). The simple predator/prey ratio allows us to determine contaminant transfer on a congener level. The resulting ratios (Figs. 48-50) show no distinct variation with K_{ow}. In addition, no consistent pattern by season or zone was observed on a congener specific level.

The predator/prey ratio of total PCB concentrations were 1-2 for both fall and spring channel catfish vs. prey fish and fall white perch vs. invertebrates (Fig. 29). The predator/prey ratios for spring channel catfish and white perch vs. invertebrates were higher due to low lipid content in spring invertebrates. Invertebrate spawning dynamics influence lipid content, thereby altering trophic transfer ratios (Wilhelm 2002).

Our results do not support the theory of increased biomagnification with higher trophic levels in the Delaware River estuary (Oliver and Niimi 1988; VanderZanden and Rasmussen 1996). Little magnification occurs between trophic levels as seen with predator/prey ratios of around 1 for both channel catfish and white perch over the range of PCB congeners. Previous work suggested that trophic transfer ratios decrease with increasing K_{ow} due to reduced uptake and assimilation efficiencies of highly chlorinated congeners (Thomann 1989; Kannan et al. 1997; Maruya and Lee 1998)

Although predator/prey ratios give insight into the transfer of contaminants, multiple prey items are not taken into account into this ratio. Channel catfish are opportunistic feeders; therefore narrowing prey items to one or two species overlooks the actual consumption patterns and levels seen in gut content analyses seen by Horwitz et al., 2002. Channel catfish may consume macrobenthic invertebrates such as crayfish and crabs; these prey items may be used to examine predator/prey ratios but do not compose the entire diet of higher trophic levels.

Using PPRs, seasonal and spatial variability in consumption is also not expressed accurately. In estuarine environments, consumption patterns may be affected by presence of prey items due to the salinity gradient as well as seasonal constraints. For example, grass shrimp were collected and subsequently analyzed in Zone 5 during the fall campaign. Due to the salinity gradient in the river and limited sampling capabilities, grass shrimp were not collected upstream of Zone 5. In both spring and fall, gut content analyses (Horwitz et al., 2002) revealed a greater proportion of these prey in the stomachs of both perch and catfish in Zone 5. Using the lipid normalized t-PCB concentration found for this prey item, PPR for catfish/shrimp and perch/shrimp in Zone 5 were calculated to be 3.6 and 1.0, respectively.

Other difficulties in assessing the trophic transfer of PCBs from the potential prey items arise. In fall and spring sampling campaigns, insufficient numbers of macrobenthic prey items were collected. Moreover, in the upper zones of the estuary, algae were found in the guts of channel catfish. It is not known whether algae are ingested as food or ingested as a by-product in the foraging of benthic organisms such as amphipods. The role of algae in delivering contaminants to the fish is not known. Benthic algal mats and periphyton may well represent a significant source of carbon and associated PCBs to catfish in this zone. Unfortunately, no algae biomass was collected in this study. The paucity of PCB data for these potential prey items again further complicates the full assessment of trophic transfer of PCBs to predators such as catfish and perch. Future studies regarding food web dynamics should further examine lower trophic levels both spatially and temporally.

Congeneric Pattern Differences

By quantifying the similarities and differences in accumulated patterns between fish collected from various locations, some insight into the factors controlling bioaccumulation may be gained. Because of their limited home-range and diet consisting partially of benthos such as amphipods and other bethic or epi-benthic prey items, it is not surprising that accumulated PCB patterns in catfish are more reflective, both magnitude and congener wise, of the sediment. The increases in concentrations of the more chlorinated congeners such as PCB 209 with down-river catfish collections was also observed in their prey items in addition to the sediment in which they are closely coupled. A study in the Potomac River showed that PCB congener profiles of catfish collected in regions less than 3-4 Km showed significant pattern differences between zonal collections in that sub-estuary, again supporting the notion that this species may be indicative of local contamination (unpublished data, Baker).

Contrast this with the magnitude and patterns observed in white perch. On average, lipid normalized concentrations in this species were lower and congeneric patterns less closely matched benthic prey items and sediment. In contrast to catfish that may only integrate benthic PCB inventories on limited spatial scales, white perch are likely integrators over larger spatial scales. Moreover, their migration behavior is dependent upon season, enhancing their ability to integrate over even larger scales. Tagging data in the Patuxent River, MD, indicated that white perch sample local conditions during summer, fall, and winter months (Mansueti, 1961). During these months, greater than 75% recaptured white perch were recaptured within 16 km of their release location. Unfortunately, no comparable tagging study exists for Delaware River estuary white perch, but the Mansueti (1961) study indicated that white perch captured during summer, fall, and winter sampled local conditions. However, in spring, white perch captured within the

Delaware zones likely represent a spawning contingent that includes fish that had sampled the entire Delaware Estuary.

The presence of congener 209 (a surrogate for the general enrichment of more chlorinated congeners in the benthic environment in down-river zones) was so striking in all biota except for perch that this may be helpful in deciphering how predators such as perch and catfish bioaccumulate PCBs. In fall, white perch had low and unvariable concentrations of 209 between zones. This may be reflective of dietary shifts between the zones. In comparison to white perch, channel catfish are expected to more accurately reflect local sediment and macrobenthos PCB inventories. Moreover, specific congeners (e.g., PCB 206 and 209) may act as indicators of specific and unique local contamination with sub-zones of the Delaware River estuary.